Sens. & Instrumen. Food Qual. (2009) 3:100–107
DOI 10.1007/s11694-008-9064-y

ORIGINAL PAPER

Feasibility of colloidal silver SERS for rapid bacterial screening

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Received: 5 June 2008 / Accepted: 31 October 2008 / Published online: 20 November 2008

Abstract This study reports the feasibility of citrate-reduced colloidal silver surface-enhanced Raman scattering (SERS) for differentiating three important food borne pathogens, *E. coli*, *Listeria*, and *Salmonella*. FT-Raman and SERS spectra of both silver colloids and colloid-K_3PO_4 mixtures were collected and analyzed to evaluate the reproducibility and stability of silver colloids fabricated in a batch-production process. The results suggest that the reproducibility of the colloids over the batch process is high and that their binding effectiveness remains consistent over a 60-day storage period. Two specific SERS bands at 712 and 390 cm^{-1} were identified and used to develop simple 2-band ratios for differentiating *E. coli*-, *Listeria*-, and *Salmonella*-colloid mixtures with a 100% success. These results indicate that colloidal silver SERS technique may be a practical alternative method suitable for routine and rapid screening of *E. coli*, *Listeria*, and *Salmonella* bacteria.

Keywords SERS · Silver colloid · *E. coli* · *Listeria* · *Salmonella* · Food safety

Introduction

The high sensitivity of surface-enhanced Raman scattering (SERS) spectroscopy for even trace amounts of specific analytes has led to its development as an extremely powerful analytical tool for a wide range of applications, including defense, environmental, and biomedical sensing. SERS enables identification of specific chemical compounds by their vibrational spectroscopic characteristics [1]. Recent research has investigated methods of surface enhancement and the use of SERS for identifying specific chemical and biological analytes, including bacteria and viruses [2–8]. In order to achieve SERS signal enhancement, the analyte must be attached (adsorbed) or in close proximity to a specially prepared surface of a noble metal, such as gold (Au) or silver (Ag). Currently, a number of different types of Au and Ag substrates have been developed, in the forms of metal colloids, roughened electrodes, nanorod arrays, and vacuum-deposited metal/nanoparticle island films [2–11]. In particular, the use of silver colloids has been investigated in many studies [2, 3, 6, 7]. Silver colloids have several advantages over other substrates: (i) they can be easily and inexpensively prepared by reduction of aqueous solution of silver salts; (ii) the silver nanoparticles are suspended in solution and can slow their oxidation process, meaning that a fresh surface is available for each analysis and their lifetime can be long; (iii) silver colloids provide homogeneous binding sites between nanoparticles and analyte; and (iv) the optical properties of silver colloids can be easily evaluated by UV–visible spectroscopy. However, like other substrates, there are still problems associated with the reproducibility and stability of silver colloids. Silver nanoparticles might vary from batch to batch in the size, shape, distribution, and aggregation of particles, and also tend to aggregate and to precipitate in solution over time [6, 11].

A preliminary investigation established procedures for the use of colloidal silver SERS in the routine and rapid identification of *E. coli*, and *Listeria* bacterial cultures [12]. SERS biomarkers were identified for the target bacteria, and detection algorithms utilizing two-waveband ratios

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were developed. In that study, a simple sampling method mixed the silver colloid with incubated bacteria culture samples directly in glass cuvettes, which reduced the possibility of bacterial cross-contamination during the analysis process. This SERS procedure may be a useful tool to complement traditional antibody- and nucleic-acid-based analysis methods [13, 14], which have already been developed as viable tools to identify bacteria but are labor-intensive multi-step procedures requiring species-specific antibodies and/or probe reagents.

This study further investigates the SERS technique of the previous study, (i) to perform a more thorough evaluation of the reproducibility and stability of silver colloid batch production and storage, (ii) to identify and verify biomarkers for one additional target bacteria—*Salmonella*—as well as for *E. coli* and *Listeria*, and (iii) to verify the effectiveness of the two-band ratio detection algorithm for these three bacteria types.

Materials and methods

Chemical reagents and glass tubes

Chemical reagents (silver nitrate, >99%; trisodium citrate, >99%; and tripotassium phosphate, >98%; Sigma-Aldrich Co., St. Louis, MO, USA) and Trypic Soy Broth (TSB) growth media (Becton, Dickinson and Co., Sparks, MD, USA) were used without further purification. Disposable glass tubes (6 mm in outside diameter × 50 mm in length) were supplied by Fisher Scientific (Suwanee, GA, USA).

Silver colloids

During a fourteen-month period, thirteen batches of citrate-reduced colloidal silver suspensions were prepared by a modified Lee and Meisel procedure [15]. The procedure for each batch is summarized briefly as follows: A sterilized 250 mL beaker containing 100 mL of distilled/deionized water and a magnetic stir bar was covered with aluminum foil (to minimize evaporation) and placed on a hot plate. After heating to approximately 45 °C, 18 mg of silver nitrate was added to the beaker. With further heating and stirring, the solution was brought to boiling and 2 mL of 1% (w/v) trisodium citrate was introduced. With continuous stirring, the solution was boiled for about 15 min to allow sufficient time for the formation of silver colloidal nanoparticles, which resulted in a gradual color change in the solution from colorless to a gray/green appearance approximately 7 min after adding the trisodium citrate. The beaker was removed from the heat and cooled to room temperature. Each batch of colloidal silver was used directly for FT-Raman spectroscopy, either alone or with a target analyte, without further modification of the nanoparticle surfaces or addition of aggregation agents.

Bacterial cultures

Multiple batches were prepared for each of the three bacteria types, *Escherichia coli, Listeria monocytogenes, and Salmonella typhimurium.* Over a span of 14 months, 17 batches of *E. coli* ATCC 25922, 16 batches of *L. monocytogenes* ATCC 13932, and 15 batches of *S. typhimurium* ATCC 14028, were incubated overnight in TSB media at 37 °C for approximately 17–20 h without agitation. This growth procedure routinely yielded a culture containing $\sim 10^9$ colony forming units (CFU)/mL of each bacterium at stationary phase. The incubated cultures were analyzed with no further treatment.

SERS spectral collection and interpretation

SERS spectra were collected on a Nexus 670 FT-IR bench with Raman module (Nicolet, Madison, WI, USA). The Raman module includes an InGaAs detector and XT-KBr beamsplitter. Each aqueous sample (colloid alone or analyte/colloid mixture) was placed in a 6 × 50 mm (O.D. × L) glass tube and illuminated using the 1064 nm Nd:YAG excitation laser. Raman scatter was accumulated using 180° reflective mode with 1 W of laser power and 256 scans at 8 cm−1 resolution. All spectral data were smoothed with a second-order Savitzky–Golay polynomial with 11 point gap, using Grams/32 software (Version 7.0, Galactic Industries Corp., Salem, NH, USA).

Spectral measurements were acquired for samples of silver colloid alone, for mixtures of silver colloid mixed with aqueous solution of K_3PO_4 (1.0×10^{-2} M), and for mixtures of silver colloid with each of the three aqueous TSB bacterial cultures. To evaluate reproducibility and stability of the silver colloids over time, comparison of spectra for 50 μL samples from each of the 13 batches of colloidal silver when fresh and after 13 weeks of storage was performed. To measure binding effectiveness of the silver colloids as well as reproducibility and stability, 40 μL of silver colloid were mixed with 40 μL of aqueous K_3PO_4 (final K_3PO_4 concentration of 5×10^{-3} M) and SERS spectra were acquired for these samples approximately once per week over a 90 day period. To identify and verify biomarkers for samples of silver colloid mixed with TSB bacterial cultures, 40 μL volumes of silver colloid were mixed with 40 μL of TSB bacteria culture for spectral measurement. For all mixture samples, the glass tube was harshly shaken 5 times and then rested for 10 min prior to spectral measurements.

Results and discussion

Assessment of reproducibility, stability, and binding effectiveness of batch based silver colloids

Figure 1a shows the mean Raman (1,700–100 cm^{-1}) spectrum with standard deviation envelope calculated from the spectra of the 13 batches of freshly prepared silver colloid. Before taking the mean, the 13 spectra were normalized at 215 cm^{-1} peak by scaling its maximum intensity to be one. It can be seen that the 215 cm^{-1} band is the only significant peak; no other peaks arise from decomposed chemical residuals and water in silver colloids.

As a comparison, Fig. 1b shows the mean Raman spectrum with standard deviation envelope calculated for normalized spectra of the thirteen batches of silver colloid after 90 days. Again, no additional SERS peaks are observed for the silver colloids during 13-week storage at room temperature except the band at 215 cm^{-1}. This suggests that the silver colloidal suspensions are stable and this result is consistent with that of other reports [11, 16].

For this study, K_3PO_4 was selected as a target analyte because of its characteristic P–O vibrations [12]. Figure 2 shows typical spectra for (a) a sample of aqueous K_3PO_4 solution (1.0×10^{-2} M), (b) a sample mixture of aqueous K_3PO_4 solution mixed with silver colloid suspension, and (c) a sample of solid state K_3PO_4. The phosphate bands are clearly surface-enhanced by the silver colloid, appearing much more intense in curve for the colloidal silver mixture (b) than in curve for the aqueous solution (a). Three intense bands at 1,086, 922, and 564 cm^{-1} are exhibited in the SERS curve. In comparison, the FT-Raman spectrum of K_3PO_4 in solid state (c) is dominated by a very strong band near 922 cm^{-1}, which arises from the symmetric P–O stretching mode (ν_1) [17, 18], while other bands are evident but at much lower intensity. Therefore, the high intensity of the ν_1 SERS P–O band at 922 cm^{-1} could be used to evaluate the binding effectiveness of silver colloidal nanoparticles in both fresh and aging state [12].

The two-waveband intensity ratio of I_{922}/I_{850} was used [12] an indicator of the binding effectiveness of silver colloidal nanoparticles with aqueous K_3PO_4. On the left

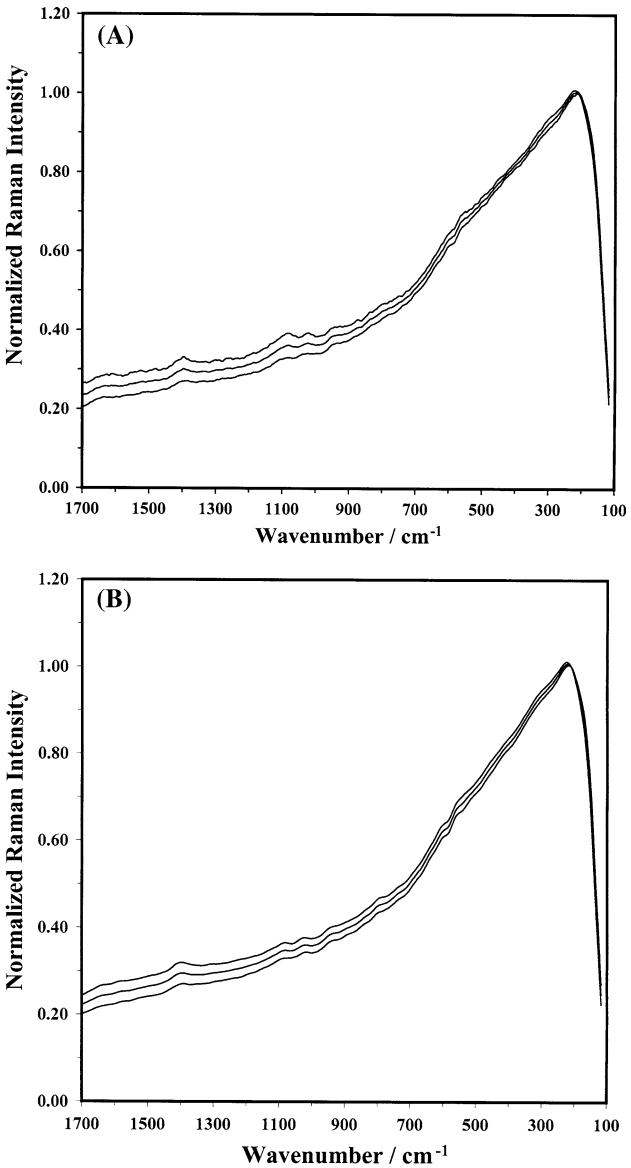

Fig. 1 **a** Average (middle) ± standard deviation (SD, upper and lower) Raman spectra of 13 fresh silver colloids prepared with a batch process. **b** Average (middle) ± SD (upper and lower) Raman spectra of silver colloidal suspensions over the 90-day storage period

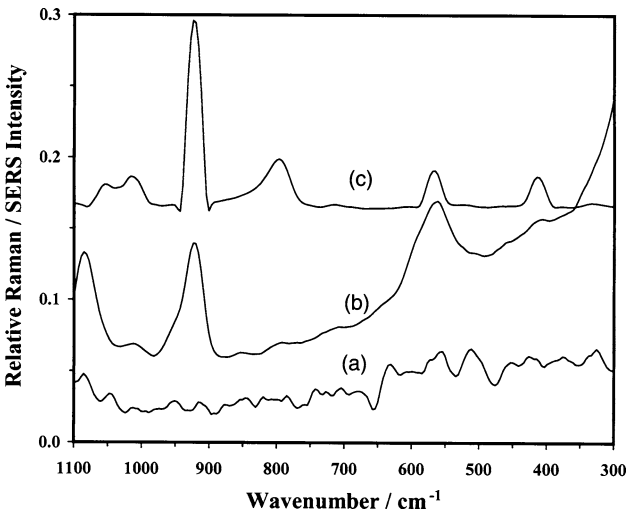

Fig. 2 **a** FT-Raman spectrum of a K_3PO_4 aqueous solution (1.0×10^{-2} M); **b** SERS spectrum of aqueous K_3PO_4 solution (final concentration of 5.0×10^{-3} M); and **c** FT-Raman spectrum of K_3PO_4 in solid state. Intensities in (**b**) and (**c**) were reduced and spectra were shifted vertically for direct comparison

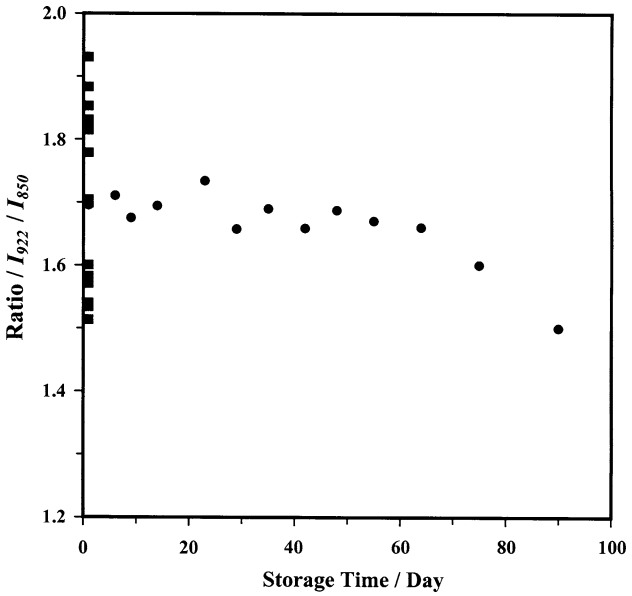

Fig. 3 Time-dependent binding effectiveness of colloidal silver nanoparticles with K_3PO_4 aqueous solution (final concentration: 5.0×10^{-3} M). Ratio values for 13 fresh colloidal batches were inserted at the most left for comparison

side of Fig. 3, the I_{922}/I_{850} ratio is plotted for fresh samples (Day 1) of the 13 colloidal silver batches (square data points). The relative standard deviation (RSD) for these 13 batch-production samples is 9.6%. This result is very close to the best reported RSD of 6.6% between the citrate-stabilized borohydride-reduced silver colloids prepared using the flow system and evaluated using azo dye [11].

The round data points on Fig. 3 show the average I_{922}/I_{850} ratio with increasing storage time, from Day 1 to Day 90. The average I_{922}/I_{850} value exhibits only a very slight decrease during the first 60 days of storage, suggesting that the binding capability of silver colloidal nanoparticles with K_3PO_4 is unaffected during this period. At the 90th day storage, binding effectiveness is reduced by only 12%. The relative standard deviation over time is only 3.5%. Apparently, binding effectiveness of the colloidal silver nanoparticles varies more greatly across separate batches than it does over storage time. The colloidal silver nanoparticles in this study show a much longer effective lifetime than that of other forms of silver used to enhance Raman spectroscopy as reported in previous studies, such as silver nanoparticle films deposited on glass slides via thermal vacuum evaporation [9] or deoxidizing silver iodide nanoparticles [19]. Li and Cullum [9] found that SERS signal intensity decreased with increasing exposure time to air, and observed a 50 and 75% decay of signal intensity after the substrates were exposed to ambient conditions for approximately 8 days and 20 days, respectively. Li et al. [19] reported that SERS enhancement increased initially, reached a maximum on about the 45th day after the preparation and then gradually decreased to 50% of maximum intensity around the 90th day.

SERS biomarkers of bacteria-colloid mixtures

Figure 4 shows example SERS spectra from two different batches of *E. coli*–silver colloid mixtures, acquired using the same procedure but 2 months apart. For comparison, the FT-Raman spectrum of a TSB-grown *E. coli* culture without silver colloid is also shown (labeled as *intact*) which exhibits no significant Raman bands. There are large variations in both relative intensity and position of SERS-active bands, because of subtle changes among silver colloidal batches and unpredicted "hot" binding sites. Since incubated bacterial cultures consist of numerous species, which were pre-existing in growth media and were produced as the byproducts during the bacterial growth, clear understanding of the origins of SERS-active bands is not straight forward.

Despite fluctuations in relative intensity and position of SERS bands for different *E. coli*–colloid mixtures, several common bands are observed with careful examination of the *E. coli*–colloid spectra. Among them, the 712 cm^{-1} band is quite interesting because it always appears as the strongest and sharpest. Further dilutions of the *E. coli* suspensions were prepared, created by adding either more TSB growth medium or silver colloid. The SERS spectra

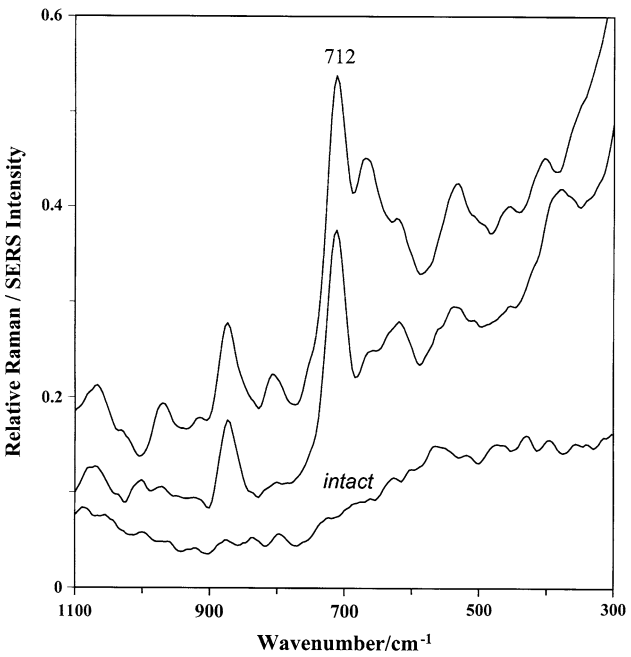

Fig. 4 SERS spectra of two *E. coli*–colloid mixtures, compared with an FT-Raman spectrum of *E. coli* culture sample (*intact*). Two SERS spectra were shifted vertically for direct comparison

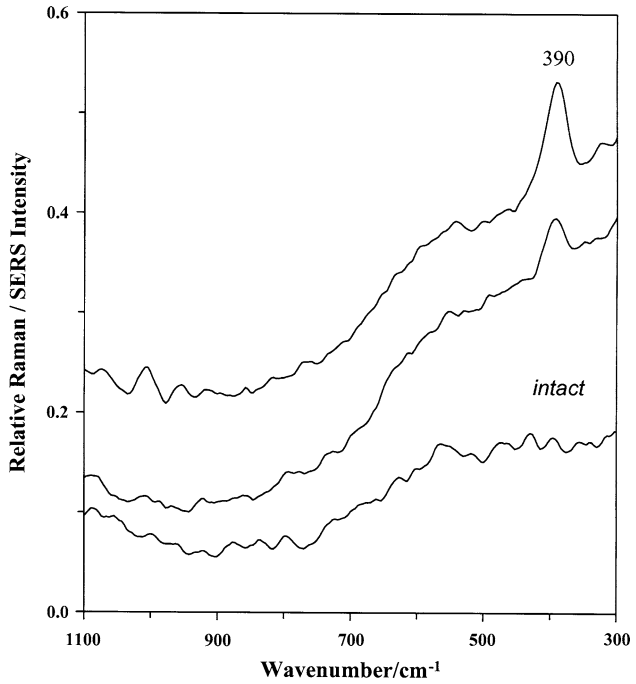

Fig. 5 FT-Raman spectrum of *Listeria* culture (marked as *intact*) and SERS spectra of two *Listeria*–colloid mixtures. SERS spectra were shifted vertically for direct comparison

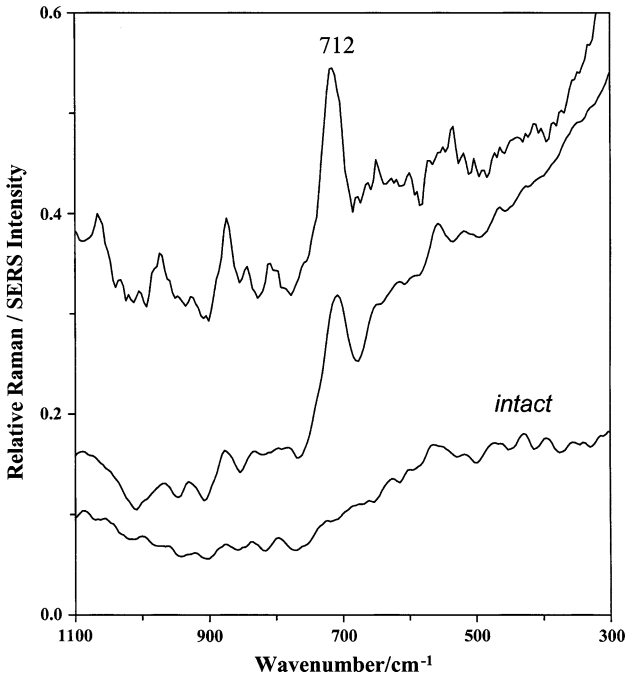

Fig. 6 FT-Raman spectrum of *Salmonella* culture (marked as *intact*) and SERS spectra of two *Salmonella*–colloid mixtures. SERS spectra were shifted vertically for direct comparison

for these diluted samples were examined and consistently showed a dominant 712 cm^{-1} peak. Therefore, the 712 cm^{-1} band could be one of most important biomarkers for identifying *E. coli* cultures using SERS spectroscopy.

The FT-Raman spectrum of *Listeria* culture and the SERS spectra of two *Listeria*–colloid batches are shown in Fig. 5. Similar to the observations in Fig. 4, Fig. 5 shows some differences in both relative intensity and position of SERS-active bands. However, the *Listeria*–colloid mixture spectra always exhibit a 390 cm^{-1} band that is the strongest and best separated, indicating that this 390 cm^{-1} band might be useful for the identification of *Listeria* suspensions.

FT-Raman spectrum of *Salmonella* culture and the SERS spectra of two *Salmonella*–colloid batches are given in Fig. 6. The *Salmonella*–colloid spectra show a strong SERS peak at 712 cm^{-1}, much like the SERS spectra for *E. coli*–colloid mixtures, but lack the 390 cm^{-1} peak exhibited by the *E. coli*– and *Listeria*–colloid mixtures. Close examination of the SERS spectra for all bacteria–colloid mixture samples, replicated in multiple batches over a 14-month period, indicated that the intense 712 cm^{-1} SERS peak is common to *E. coli* and *S. typhimurium* colloid suspensions and thus could be used to differentiate these two cultures from *L. monocytogenes* cultures. The 390 cm^{-1} SERS band is indicative of *L. monocytogenes* cultures but also could be used separately to discriminate *E. coli* cultures from *S. typhimurium* cultures.

Variation in SERS two-band ratios for bacteria–colloid mixtures

Figure 7 shows the SERS two-band ratio values using the intensities at 712 and 730 cm^{-1} (I_{712}/I_{730}), and at 390 and 352 cm^{-1} (I_{390}/I_{352}), for the 17 batches of *E. coli*–colloid mixtures. Each data point represents the average ratio for

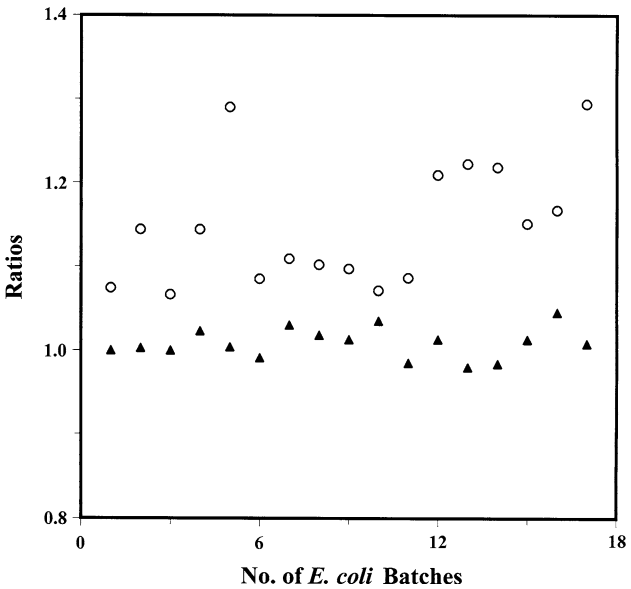

Fig. 7 *E. coli*–colloid mixture batch-dependent variations of ratio values, I_{712}/I_{730} (○) and I_{390}/I_{352} (▲)

two bacteria–colloid mixtures prepared from the same *E. coli* culture but using two different batches of silver colloid. The I_{712}/I_{730} ratio shows greater variation than the I_{390}/I_{352} ratio, but the I_{712}/I_{730} values are all greater than 1.05 for the *E. coli*–colloid mixtures.

Figure 8 shows the ratio values for 16 *Listeria*–colloid mixtures using the same two SERS ratios, I_{712}/I_{730} and I_{390}/I_{352}. In contrast to the *E. coli*–colloid mixtures, these *Listeria*–colloid samples show higher I_{390}/I_{352} ratio values than I_{712}/I_{730} ratio values. In this case, the I_{712}/I_{730} values are all below 1.05.

Figure 9 shows the ratio values for 15 *Salmonella*–colloid mixtures using the same two SERS ratios. The *Salmonella* mixtures all show I_{712}/I_{730} ratio values greater than 1.00 and I_{390}/I_{352} ratio values less than 1.00.

Variations of growth media batches

SERS spectra and ratio values were also calculated for silver colloid alone and for mixtures of TSB growth media with silver colloid, both without the addition of any bacterial cultures. Figure 10 shows a representative SERS spectum for TSB growth media, which consists of a mixture of organic and inorganic nutrients. No significant SERS bands are exhibited. Figure 11 shows I_{712}/I_{730} ratio values and I_{390}/I_{352} ratio values calculated from the SERS spectra of twenty silver colloid and TSB–colloid mixtures. It can be seen that the ratio values for TSB media and colloids all fall within a narrow range between 0.90 and 1.02.

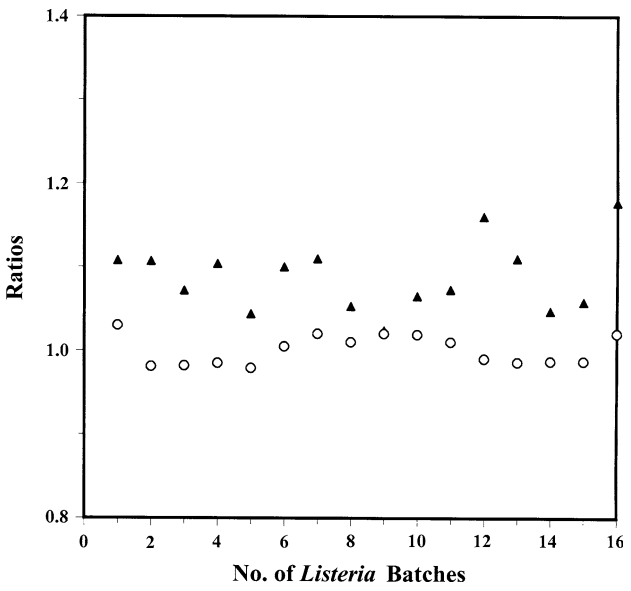

Fig. 8 *Listeria*–colloid mixture batch-dependent variations of ratio values, I_{712}/I_{730} (○) and I_{390}/I_{352} (▲)

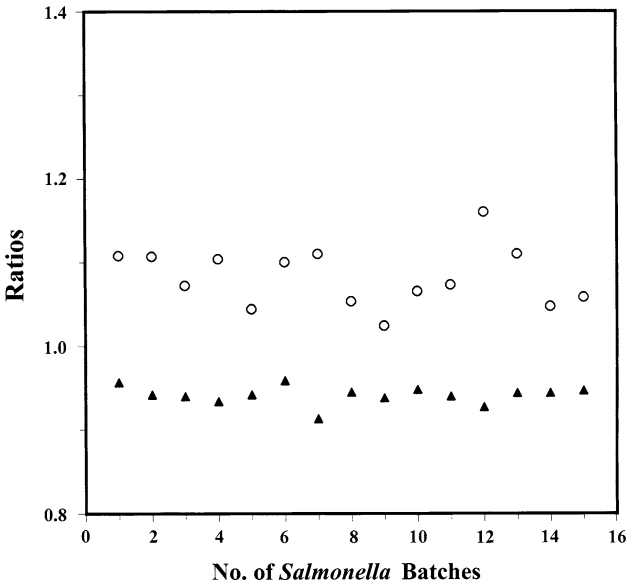

Fig. 9 *Salmonella*–colloid mixture batch-dependent variations of ratio values, I_{712}/I_{730} (○) and I_{390}/I_{352} (▲)

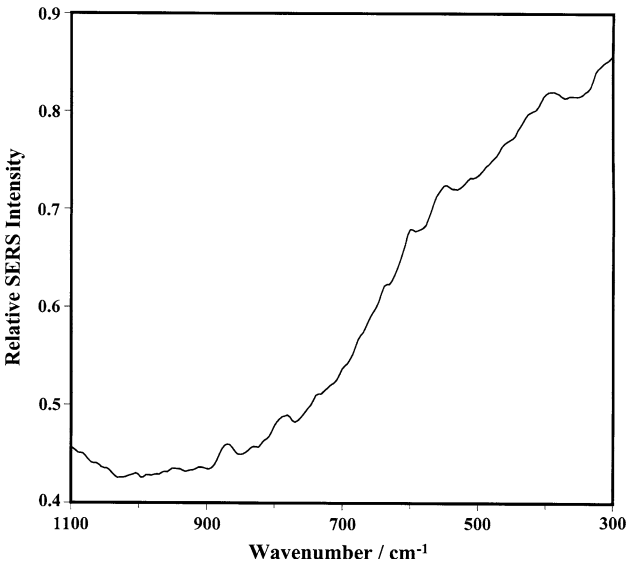

Fig. 10 Representative spectrum of TSB–colloid mixture

Identification of bacterial species

Due to the magnitude differences for the ratio values observed in Figs. 7, 8, 9, and 11, it is possible to identify the bacteria by plotting the I_{390}/I_{352} ratio values against the I_{712}/I_{730} ratio values. Figure 12 shows that excellent separation between various species is possible. The I_{712}/I_{730} ratio value of 1.04 can be used to separate *E. coli* and *Salmonella* cultures from *Listeria*, TSB growth media, and silver colloids. The I_{390}/I_{352} ratio value of 0.97 can be used to separate *E. coli* and *Salmonella* cultures from each other. The I_{390}/I_{352} ratio value of 1.02 can be used to

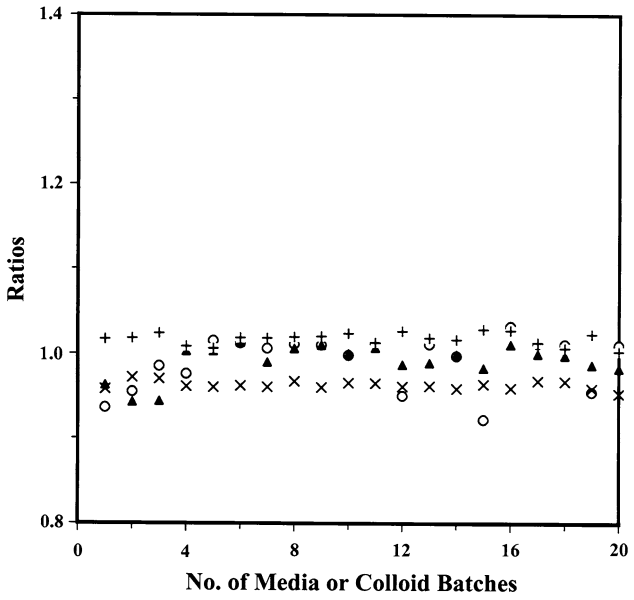

Fig. 11 TSB–colloid and colloid batch-dependent variations of ratio values, I_{712}/I_{730} (○, TSB media; +, colloid), and I_{390}/I_{352} (▲, TSB media; X, colloid)

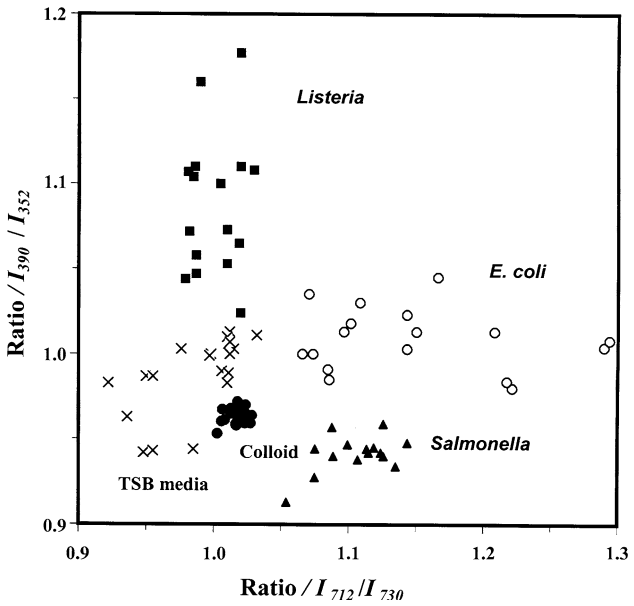

Fig. 12 Plot of the of I_{712}/I_{730} versus I_{390}/I_{352} ratio values for *E. coli*–colloid mixtures (○), *Listeria*–colloid mixtures (■), *Salmonella*–colloid mixtures (▲), TSB–colloid mixtures (X), and silver colloids (●)

separate *Listeria* from TSB growth media and silver colloids. The three bacterial cultures and the TSB growth media display wider scatter distribution than the silver colloids, probably due to a number of factors, such as the variations of chemical components and heterogeneities over batches of bacterial cultures and colloidal suspensions, colloids and bacterial culture preparation. Meanwhile, the close disposition of silver colloids suggests the reproducibility, consistency, and stability over the batch production process and over storage time. It should be noted that the samples in Fig. 12 are differentiable using SERS spectral data despite their preparation over a 14-month period using different batches of colloidal silver that may have been stored for up to 40 days before use.

Although multivariate analysis of SERS spectra has been reported to discriminate different bacterial species, previous studies used SERS data from only one colloidal batch and preprocessed the SERS spectra by subtracting a linearly increasing baseline [6]. This kind of preprocessing is poorly suited for sample-by-sample analysis and can be time-consuming. Therefore, the development of two-band ratio algorithms utilizing the unique silver-colloid based SERS biomarkers in this study presents a simple tool that can be potentially used for routine screening of *E. coli*, *Listeria*, and *Salmonella* species.

Conclusions

To examine the reproducibility, stability, and binding effectiveness of citrate-reduced silver colloids over batch production and storage process, FT-Raman spectra of colloidal silver suspensions and SERS spectra of a K_3PO_4 target compound in diluted solutions were collected. This use of K_3PO_4 can be a tool for ensuring stable quality of batch-based silver colloids for routine use over extended periods of time. The binding effectiveness of batch-produced silver colloids remains very consistent during the first 60 days of storage and shows a slight decrease with a binding reduction of about 12% at the 90th day, which is much longer than the effective binding reported for some silver nanoparticle films. Characteristic SERS bands were identified at 712 and 390 cm^{-1} for cultures of *E. coli*, *Listeria monocytogenes*, and *Salmonella typhimurium.* These SERS bands were incorporated into two-waveband ratios, I_{390}/I_{352} and I_{712}/I_{730}, that could be used to differentiate between the three bacterial cultures with 100% success.

On the basis of practical implementation, this study suggests simple procedures to produce silver colloids and assess their quality, to prepare bacterial cultures for SERS analysis, and to analyze the SERS spectra for the differentiation of *E. coli, Listeria*, and *Salmonella*. These procedures avoid the need to perform processes of labeling, purifying, separating, drying, or washing the bacterial samples, and also are advantageous in using small volumes of bacterial cultures and silver colloid and in requiring only about 20 min for bacteria–colloid mixture preparation and SERS measurement. These results suggest that colloidal silver SERS technique can be used in routine and rapid screening for *E. coli*, *Listeria* and *Salmonella* bacteria.

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